



PATENT SPECIFICATION

NO DRAWINGS

1,184,729

Date of Application and filing Complete Specification: 10 Aug. 1967

No. 36727/67

Application made in United States of America (No. 584,365) on 5 Oct. 1966

Complete Specification Published: 18 March 1970

Index at acceptance:—C1 J(4, 5, 9, 14, 19, 23, 33)

Int. Cl.:—C 04 b 35/10

COMPLETE SPECIFICATION

Composition for making Refractory Articles

We, AMSTED Industries Incorporated, 3700 Prudential Plaza, Chicago, Illinois 60601, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to a composition for making refractory articles and more particularly to a composition from which refractory pouring tubes for the pressure pouring of molten metal can be made.

Pressure pouring of molten metal is an operation in which molten metal is forced from a source below a mold, otherwise than by gravity and/or hydrostatic head in a generally upward direction into the mold in which the material solidifies or partially solidifies. The molten metal is forced upwardly from the source, such as a ladle, through a pouring tube. The pouring tube is immersed in the molten metal and is in open communication with the mold thereby providing a passage for the metal from the ladle to the mold.

Pouring tubes are formed from a highly refractory mix of alumina and silica among other components. In the past, these conventional pouring tubes have possessed a relatively low resistance to the thermal shocks encountered in pressure pouring. In conventional operations, the tubes are preheated to about 1000°C and during the cyclic pouring operations they are subjected to temperatures of in excess of 1500°C. The conventional tubes have a tendency to crack during the pressure pouring and they must be frequently replaced with the attendant increase in cost of operation.

It is therefore an object of this invention to provide a composition from which pouring

tubes of improved resistance to thermal shock may be produced.

Another important object of this invention is to provide such a composition whereby the tubes made therefrom having improved thermal expansion characteristics.

A further object of this invention is to provide bottom pressure casting pouring tubes of improved service life.

Another object of this invention is to provide a composition for making pouring tubes that will withstand substantial temperature variations.

According to the present invention, the refractory articles such as bottom pressure casting pouring tubes are made from a composition comprising a mixture of dry ingredients and five to fifteen per cent, based on the weight of dry ingredients, of a colloidal silica solution, said dry ingredients comprising by weight, 10 to 30 per cent tabular alumina, 5 to 20 per cent calcined alumina, 8 to 15 per cent alpha quartz, and 0.03 to 0.2 per cent fused magnesium oxide, the remainder of said dry ingredients comprising a finely divided mixture of a fusion product comprising by weight, 30 to 60 per cent unstabilized monoclinic ZrO_2 , 10 to 20 per cent SiO_2 , and 30 to 50 per cent Al_2O_3 .

The fusion product is preferably made by melting, as in an electric arc furnace, zirconium silicate, zirconium oxide and aluminium oxide.

The tabular alumina and alpha quartz may be replaced by fifteen to thirty per cent kyanite.

The invention also provides a composition for making refractory articles high resistance to thermal shock comprising a mixture of dry ingredients and 5 to 15 per cent, based on the weight of dry ingredients, of a colloidal silica solution, said dry ingredients comprising by weight, 5 to 30 per cent of calcined alumina, 15 to 30 per cent of calcined kyanite, 0.03 to

0.2 per cent of fused magnesium oxide, the remainder of said dry ingredients comprising a finely divided mixture of a fusion product comprising by weight, 30 to 60 per cent of unstabilized monoclinic ZrO_2 , 10 to 20 per cent of SiO_2 , 30 to 50 per cent of Al_2O_3 .

The dry ingredient particles are preferably sized to provide optimum density and forming characteristics of the composition. In this preferable feature forty to fifty per cent of the particles are four to forty mesh, ten to twenty per cent are forty to two hundred mesh and thirty-eight to forty-five per cent are two hundred mesh to submicron in size. In the preferred embodiment the coarse fraction (4 to 40) is forty-five per cent, the intermediate fraction (40 to 200) fifteen per cent and the fine fraction (200 to submicron), about forty per cent. The mesh sizes are quoted on the Tyler scale.

The fusion product, tabular alumina, calcined alumina, alpha quartz, fused magnesium oxide and colloidal silica solution are thoroughly mixed in a mixing tank to which ice has been added to control the temperature and thereby the acidity of the batch. The batch is stirred in the tank until a slurry is produced having a consistency of frothy mud. The temperature of the slurry at this stage is about $12^\circ C$.

The slurry is then trickled into a vacuum chamber having a vacuum pressure of about 28 inches of mercury. This removes any air bubbles in the slurry. The slurry is then pumped into a mould having the configuration of the desired pouring tube where the slurry is heated to cause the colloidal silica solution to gel and thereby set the slurry into the configuration of the tube. After removal of at least a portion of the mould, the tube is dried at about $50^\circ C$. for six to forty hours and then fired in a kiln at $2650^\circ F$. or cone 16 for about three days for the complete firing cycle which includes about ten hours at $2650^\circ F$.

The following specific examples are included as illustrative of the compositions of this invention.

Example 1

The fusion product contained 47.6% ZrO_2 , 35.7% Al_2O_3 and 16.7% SiO_2 . About 48% of

the composition was fusion product 4 to 40 mesh, about 11% of the composition was fusion product 40 to 200 mesh and the remainder of the composition was 200 to submicron. The dry ingredients of this batch also included by weight 23.1% tabular alumina, 8.2% calcined alumina, 9.7% alpha quartz and 0.10% fused magnesium oxide. The dry ingredients were mixed with 10.1%, based on the weight of the dry ingredients, colloidal silica solution which had a specific gravity of 1.23 grams per cc. and 33% SiO_2 .

Example II

The fusion product contained 43.0% ZrO_2 , 41.6% Alumina and 15.4% silica. About 50% of the composition was fusion product 4 to 40 mesh, about 11% of the composition was fusion product 40 to 200 mesh and the remainder of the composition was 200 to submicron in size. The dry ingredients of this batch also included by weight 21.3% tabular alumina, 7.7% calcined alumina, 9.2% alpha quartz, and 0.1% fused magnesium oxide. The dry ingredients of this batch were then mixed with the same colloidal silica solution as in Example I.

Example III

The fusion product contained 47.6% ZrO_2 , 35.7% Al_2O_3 and 16.7% SiO_2 . About 48% of the composition was fusion product 4 to 40 mesh, about 11% of the composition was fusion product 40 to 200 mesh and the remainder of the composition was 200 to submicron. The dry ingredients of this batch also included by weight 21.1% calcined kyanite, 21.4% calcined alumina and 0.10% fused magnesium oxide. The dry ingredients were mixed with 10.1%, based on the weight of the dry ingredients, colloidal silica solution which had a specific gravity of 1.23 grams per cc. and 33% SiO_2 .

The composition of Example I was processed in the manner indicated above into pouring tubes, which tubes were then placed in conventional bottom pressure casting equipment and were used in the production of railway wheels. Table No. 1 illustrates the reduction in scrap obtained by the use of these tubes, none of which cracked during use. This reduction in scrap is an added benefit from the use of these tubes.

TABLE 1

No. of Heats on Tube	11 Synrox Tubes		22 Standard Tubes	
	Wheels Made	Percent Scrap	Wheels Made	Percent Scrap
1	406	7.0	822	9.7
2	404	9.1	788	14.2
3	364	14.0	340	15.6
4	337	19.6	39	77.0
5	31	48.4	None used five heats	

The pouring tubes made of the compositions of this invention exhibit substantially lower thermal stress than do conventional pouring tubes made of mullite. The degree of thermal expansion for a mullite pouring tube is 56 in/in $\times 10^{-4}$ at 1000°C. and 103 in/in $\times 10^{-4}$ at 1500°C. whereas the degree of thermal expansion for the pouring tubes of Example I is 64 at 1000°C. and 78 at 1500°C. During pressure pouring the outside of the tube above the metal is about 1000°C. and the inside which is in contact with the metal is at about 1500°C. Thus the magnitude of thermal stress for the pouring tubes of this invention is substantially lower than that for the conventional pouring tubes.

It can be seen from the foregoing that pouring tubes manufactured from the composition of this invention not only are resistant to thermal shock but also substantially lower the percentage of defective products made from bottom pressure casting. While this invention has been described with reference to pouring tubes for bottom pressure casting equipment, it should be understood that other refractory articles may be made from this composition.

WHAT WE CLAIM IS:—

1. A composition, for making refractory articles having high resistance to thermal shock, comprising a mixture of dry ingredients and five to fifteen per cent, based on the weight of dry ingredients, of a colloidal silica solution, said dry ingredients comprising by weight,

10 to 30 per cent tabular alumina,
5 to 20 per cent calcined alumina,
8 to 15 per cent alpha quartz, and
0.03 to 0.2 per cent fused magnesium oxide,

the remainder of said dry ingredients comprising a finely divided mixture of a fusion product comprising by weight,

30 to 60 per cent unstabilized monoclinic ZrO_2 ,
10 to 20 per cent SiO_2 , and
30 to 50 per cent Al_2O_3 .

2. The composition as claimed in claim 1 wherein the particle size of all the dry ingredients is from forty to fifty per cent 4 to 40 mesh, from ten to twenty per cent 40 to 200 mesh, and from thirty-eight to forty-five per cent 200 to submicron.

3. The composition as claimed in claim 2, wherein the 4 to 40 mesh size is forty-five per cent, 40 to 200 is fifteen per cent and 200 mesh to submicron is forty per cent.

4. The composition as claimed in any preceding claim wherein said fusion product is present in the amount of about fifty-nine per cent and comprises 47.6% ZrO_2 , 35.7% Al_2O_3 , and 16.7% SiO_2 .

5. The composition as claimed in any preceding claim wherein said fusion product is present in the amount of about sixty-two per cent and comprises 43.0% ZrO_2 , 41.6% Al_2O_3 and 15.4% SiO_2 .

6. The composition as claimed in claim 4 wherein said composition comprises

23.1% tabular alumina,
8.2% calcined alumina
9.7% alpha quartz,
10.1% colloidal silica solution, and
0.10% fused magnesium oxide.

7. The composition as claimed in claim 5 wherein said composition includes

21.3% tabular alumina,
7.7% calcined alumina,
9.2% alpha quartz,
10.1% colloidal silica solution, and
0.1% fused magnesium oxide.

8. A composition as claimed in any preceding claim wherein the tabular alumina and alpha quartz are replaced by 15 to 30% of kyanite.

9. A composition for making refractory articles high resistance to thermal shock comprising a mixture of dry ingredients and 5 to 15 per cent, based on the weight of dry ingredients, of a colloidal silica solution, said dry ingredients comprising by weight,

5 to 30 per cent of calcined alumina,
15 to 30 per cent of calcined kyanite,
0.03 to 0.2 per cent of fused magnesium oxide,

the remainder of said dry ingredients comprising a finely divided mixture of a fusion product comprising by weight,

30 to 60 per cent of unstabilized monoclinic ZrO_2 ,
10 to 20 per cent of SiO_2 ,
30 to 50 per cent of Al_2O_3 .

10. A composition as claimed in claim 9 wherein the composition contains 21.1% calcined kyanite and 21.4% calcined alumina.

11. A composition according to claims 1 or 9 for making refractory articles substantially as hereinbefore described.

12. A refractory article prepared from the composition claimed in any preceding claim.

13. A pouring tube for the pressure casting of metals prepared from the composition claimed in any of claims 1 to 11.

Agents for the Applicants:
STANLEY, POPPLEWELL, FRANCIS
& ROSS,

Chartered Patent Agents,
Cursitor House,
9-11 Cursitor Street,
London, E.C.4.